NASA Glenn Research Center Electrochemistry Branch Battery and Fuel Cell Development Overview

This presentation covers an overview of NASA Glenn's history and heritage in the development of electrochemical systems for aerospace applications. Current developments related to batteries and fuel cells are addressed. Specific areas of focus are Li-ion batteries and Polymer Electrolyte Membrane Fuel cells systems and their development for future Exploration missions.



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Electrochemistry Branch Overview

- GRC Electrochemistry Branch Energy Storage System Background and Heritage
- Overview of Battery and Fuel Cell Development Efforts
- Electrochemistry Branch Capabilities and Facilities



RPC Electrochemistry Branch Electrochemical Energy Storage Systems

Background and Heritage

Electrochemistry Branch - Batteries



Overview

- Batteries provide a versatile, reliable, safe, modular, lightweight, portable source of energy for aerospace applications.
- Advanced battery technologies are needed to meet the challenges of future NASA missions

Experience

- Lead battery development effort for Exploration Technology Development and Demonstration Program, High Efficiency Space Power Systems
- Developed and validated component and advanced designs of Ni-Cd and Ni-H₂ cells adopted by NASA, cell manufacturers and satellite companies.
- Developed lightweight nickel electrodes, bipolar nickel hydrogen battery designs
- · Evaluated flight battery technologies for ISS
- •Jointly sponsored and conducted Li-ion battery development program with DoD that developed Li-Ion cells used on Mars Exploration Rovers
- ·Lead NASA Aerospace Flight Battery Systems Working Group –agency–wide effort aimed at ensuring the quality, safety, reliability, and performance of flight battery systems for NASA missions.
- Conducted electric vehicle battery programs for ERDA/DOE

Products/Heritage

Li-lon: Lithium-lon

Ni-Cd: Nickel-Cadmium

Ni-H₂: Nickel-Hydrogen

Ni-MH: Nickel-metal hydride

Ni-Zn: Nickel-Zinc

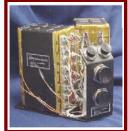
Ag-Zn: Silver-Zinc

Na-S - Sodium Sulfur

LiCFx: Lithium-carbon monoflouride







Electrochemistry Branch Fuel Cells and Regenerative Fuel Cells



Overview

- Fuel cells provide a primary source of power that can support a wide range of aerospace applications.
- Regenerative fuel cells combine a fuel cell with an electrolyzer that is capable of converting the fuel cell products into reactants when energy is supplied.
- Fuel cell /electrolysis based systems are enabling for various aspects of future NASA missions.

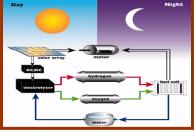
Experience

- Lead fuelcell/electrolysis development effort for Exploration Technology Development and Demonstration Program, High Efficiency Space Power Systems Project
- · Gemini, Apollo, and Shuttle technology development
- •Terrestrial energy program management for Fuel Cell systems for Stand Alone Power
- SOFC and PEM Fuel Cell development for aeronautics applications
- · Alkaline fuel cell upgrades for Shuttle
- PEM powerplant development for launch vehicles
- Fuel cell demonstration for high altitude scientific balloons, Helios
- RFC Development for High Altitude Airships
- Conducted first ever demonstration of a closed loop hydrogen-oxygen regenerative fuel cell system

Products/Heritage

AFC - Alkaline Fuel Cell
PEM - Proton Exchange Membrane
SOFC - Solid Oxide Fuel Cell
RFC - Regenerative Fuel Cell Systems







Enabling Technology Development and Demonstration Program High Efficiency Space Power Systems



Fuel Cells and Space Rated Lithium-Ion Batteries

electrochemical energy storage devices to meet power requirements and enable various mission scenarios

Fuel Cells for Surface Systems:

Proton Exchange Membrane (PEM) fuel cell technology offers major advances over existing alkaline fuel cell technology

Objective: Develop Proton Exchange Membrane (PEM) Fuel Cell technology with enhanced safety, longer life, lower mass and volume, higher peak-to-nominal power capability, higher reliability compared to alkaline fuel cells

Customers: Landers, Rovers, Orbiters

Space Rated Lithium Ion Batteries:

Lithium ion battery technology offers lower mass & volume, wider operating temperature range than alkaline battery chemistries (Ag-Zn, Ni-H2, Ni-Cd, Ni-MH)

Objective: Develop human-rated Li-ion batteries having high specific energy, energy density, long calendar life

Customers: Landers, EVA, rovers, base power, orbiters.

Overall Objectives:

- · Mature advanced technologies to TRL 6
- Integrate component technologies into prototype systems to validate performance
- •Transition technology products to future Exploration Missions





Participants:

GRC - Lead _Fuel Cells: JSC, JPL, KSC Batteries: IPL, ISC

Industry Partners, SBIR Partners, IPP Partners



Li-Ion Cell/Battery Development

Li-Ion Battery Development



Objectives: Develop Flight Qualified, Human-Rated Li-Ion cells with increased safety and reliability and mass and volume reductions

Approach:

- Identify chemistries most likely to meet overall NASA goals and requirements within allotted development timeframe
 - "High energy" and "ultra high energy" chemistries identified and targeted to meet customer requirements.
- Utilize in-house and NRA Contracts to support component development
 - Develop components to increase specific energy (anode, cathode, electrolyte)
 - Develop low-flammability electrolytes, additives that reduce flammability, battery separators and functional components to improve human-safety;
- Engage industry partner multi year contract
 - Provide recommendations for component development and screening
 - Scale-up components
 - Manufacture evaluation and screening cells
 - Design and optionally manufacture flightweight cells that address NASA's goals
- Complete TRL 5 and 6 testing at NASA
- Leverage outside efforts
 - SBIR/IPP efforts, DoE and other government programs
- Cell development TRL definitions

 TRL 4: Advanced cell components
 integrated into a flight design cell
- TRL 5: Performance testing on integrated cell shows goals met
- TRL 6: Environmental testing on cell (vibration, thermal) shows robust performance

Chemistry Identification – Feasibility Study to Determine Ultra High Energy Chemistry



Customers' top priority is <u>safety</u>.

Based on customer requirements, team determined safety goals: No fire or thermal runaway at the component level

No chemistry exists that can meet customers' aggressive specific energy goals. Desire for a safer chemistry presents a set of conflicting objectives – Safer chemistry combined with ultra high specific energy

In 2008 a feasibility study was initiated to determine the best advanced chemistry to meet EVA and Altair's requirements on the established schedule (in time for customer System Design Reviews) and within available resources.

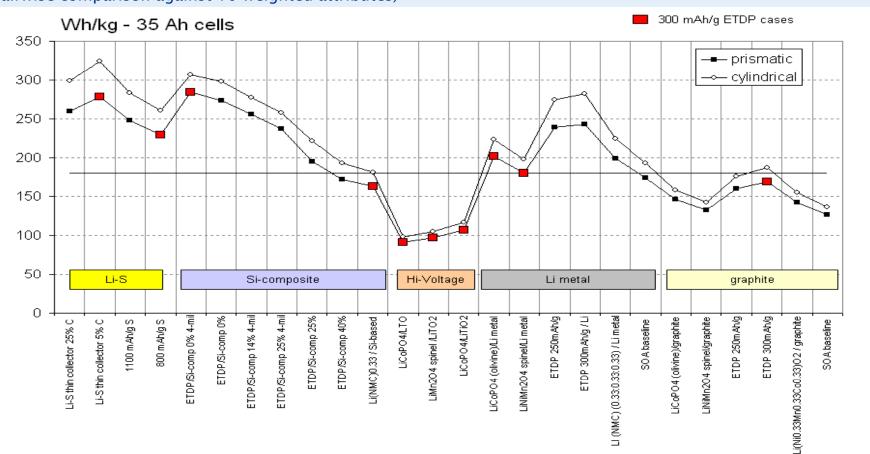
Ultra High Energy Battery Chemistry Determination

Study Goal:

Determine the best advanced chemistry to develop for EVA and Altair who require safe, reliable energy storage systems with extremely high specific energy as compared to today's state-of-the-art (SOA) batteries.

<u>Safety target:</u> No fire or thermal runaway at the component level.

<u>Specific energy target:</u> 160-220 watt-hours per kilogram delivered at the battery level at C/10 and 0°C. <u>Process:</u> Assessed 31 chemistries, selected 7 as feasible, ranked those 7 using an Analytical Hierarchy Process (pairwise comparison against 10 weighted attributes)



Attributes and Relative Rankings

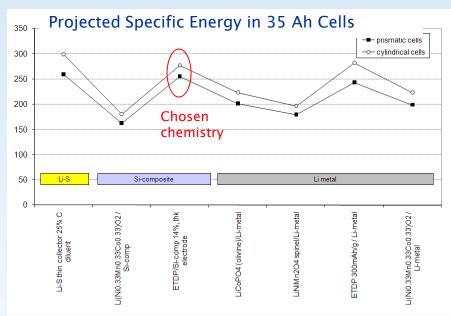


Attribute	Final Weight	Definition
Safety	17.9	The likelihood that a cell made from these components can be made to be safe. Included safety under normal operation and abuse conditions
Rate Capability up to C/5	15.6	Likelihood that the technology can meet a C/5 continuous discharge rate
Specific Energy	15.0	Projected specific energy of the technology (calculated under a standard set of conditions)
Storage and Calendar Life	12.2	Projected storage + calendar life, where calendar life includes the operating time plus periods at open circuit between active charging and discharging
Energy Density	10.2	Projected energy density of the technology (calculated under a standard set of conditions)
Manufacturability	8.3	The projected level of ease or difficulty associated with working with materials, scaling up batches of materials, and manufacturing cells of practical capacity made from these components, and the projected adaptability of materials to large scale processing
Schedule	8.0	Likelihood that TRL 6 cells can be delivered by March 2104
Cost to TRL 6	6.5	The cost to develop the technology to TRL 6, including costs attributed to costly manufacturing processes or processes that cannot be automated
Cycle Life	3.8	Projected cycle life of the technology
Rate Capability up to C/2	2.5	Likelihood that the technology can meet a C/2 continuous discharge rate



Advanced Chemistry Options and Ranking

Cathode	Anode	Rank
Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	Si-based Composite	20.2
Li(LiNMC)O ₂ (ETDP)	Si-based Composite	17.0
LiNiMn ₂ O ₄	Li metal	15.3
Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	Li metal	13.9
Li(LiNMC)O ₂ (ETDP)	Li metal	13.1
(Li ₂)S	Li metal	11.5
LiCoPO ₄	Li metal	9.1



- •Li(NMC) cathode with Si-based composite anode offers:
 - · Higher safety, manufacturability and rate capability
 - Lower specific energy
- •Li(LiNMC) (ETDP) cathode with Si-based composite anode offers:
 - Higher specific energy
 - ·Lower safety, manufacturability and demonstrated rate capability

✓ETDP cathode with Si-based composite anode chosen as Ultra High Energy chemistry due to its potential to achieve much higher specific energy.

Key Performance Parameters for Battery Technology Development

Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/control- lers used to prevent unsafe conditions. There is no non- flammable electrolyte in SOA	Preliminary results indicate a small reduction in performance using safer electrolytes and cathode coatings	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***
Specific energy Lander: 150 – 210 Wh/kg 10 cycles	Battery-level specific energy* [Wh/kg]	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	160 at C/10 & 30°C (HE) 170 at C/10 & 30°C (UHE) 80 Wh/kg at C/10 & 0°C (predicted)	135 Wh/kg at C/10 & 0°C "High-Energy"** 150 Wh/kg at C/10 & 0°C "Ultra-High Energy"**	150 Wh/kg at C/10 & 0°C "High-Energy" 220 Wh/kg at C/10 & 0°C "Ultra-High Energy"
Rover: 160-200 Wh/kg 2000 cycles	Cell-level specific energy [Wh/kg]	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	199 at C/10 & 23°C (HE) 213 at C/10 & 23°C (UHE) 100 Wh/kg at C/10 & 0°C (predicted)	165 Wh/kg at C/10 & 0°C "High-Energy" 180 Wh/kg at C/10 & 0°C "Ultra-High Energy"	180 Wh/kg at C/10 & 0°C "High-Energy" 260 Wh/kg at C/10 & 0°C "Ultra-High Energy"
270Wh/kg 100 cycles	Cathode-level specific capacity [mAh/g]	180 mAh/g	252 mAh/g at C/10 & 25°C 190 mAh/g at C/10 & 0°C	260 mAh/g at C/10 & 0°C	280 mAh/g at C/10 & 0°C
	Anode-level specific capacity [mAh/g]	280 mAh/g (MCMB)	330 @ C/10 & 0°C (HE) 1200 mAh/g @ C/10 & 0°C for 10 cycles (UHE)	600 mAh/g at C/10 & 0°C "Ultra-High Energy"	1000 mAh/g at C/10 0°C "Ultra-High Energy"
Energy density Lander: 311 Wh/l	Battery-level energy density	250 Wh/I	n/a	270 Wh/I "High-Energy" 360 Wh/I "Ultra-High"	320 Wh/I "High-Energy" 420 Wh/I "Ultra-High"
Rover: TBD EVA: 400 Wh/I	Cell-level energy density	320 Wh/I	n/a	385 Wh/I "High-Energy" 460 Wh/I "Ultra-High"	390 Wh/I "High-Energy" 530 Wh/I "Ultra-High"
Operating environment	Operating Temp	-20°C to +40°C	0°C to +30°C	0°C to 30°C	0°C to 30°C

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

0°C to 30°C,

Vacuum

^{*} Battery values are assumed at 100% DOD, discharged at C/10 to 3.0 volts/cell, and at 0°C operating conditions

^{** &}quot;High-Energy" = mixed metal oxide cathode with graphite anode

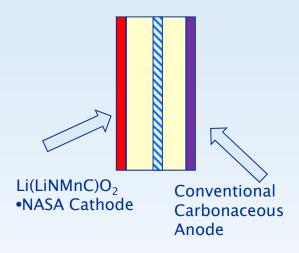
^{** &}quot;Ultra-High Energy" = mixed metal oxide cathode with Silicon composite anode

^{***} Over-temperature up to 110°C; reversal 150% excess discharge @ 1C; pass external and simulated internal short tests; overcharge 100% @ 1C for Goal and 80% @ C/5 for Threshold Value.

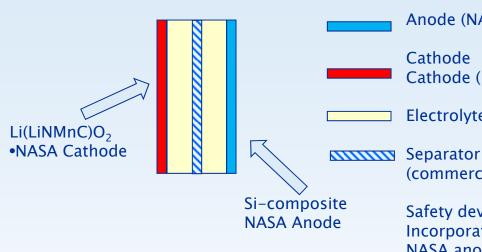
Advanced Li-Ion Battery Cell Development



High Energy Cell



Ultra-High Energy Cell



Anode (commercial)

Anode (NASA)

Cathode Cathode (NASA)

Electrolyte (NASA)

(commercial)

Safety devices (NASA) Incorporated into NASA anode/cathode

Lithiated-mixed-metal-oxide cathode - Li(LiNMnC)O₂

Conventional carbonaceous anode

180 Wh/kg @ cell level 150 Wh/kg @ battery-level At 0°C C/10

~2000 cycles to 80% of original capacity at 100% DOD

Lithiated-mixed-metal-oxide cathode -Li(LiNMnC)O₂

Silicon composite anode

260 Wh/kg @ cell level 220 Wh/kg @ battery-level At 0°C C/10

~200 cycles to 80% of original capacity at 100% DOD

Lithium Ion Battery Technology Development Advanced Cell Components

Charger or Load Nano-particle based circuit breaker Cathode Anode Collector Separator Silicon nano-particles alloy with Li during charge, lose Li ions during discharge Offers dramatically improved capacity over carbon standard

> Advanced electrolyte with additives provides flame-retardance and stability at high voltages without sacrificing performance. Example: LiPF₆ in EC+EMC+TPP+VC

- Porous, elastomeric binder allows ionic transport and accommodates large volume changes during charge/discharge cycling
- Functionalized nanoparticles adhere to binder without blocking reactive silicon surface area

Layered Li(NMC)O₂ cathode particle

 Varying composition and morphology to improve capacity and charge/discharge rate

Li-Metal-PO₄

Safety Coating for Thermal Stability

Optimized Solid-Electrolyte interface Layer

Mitigates causes of irreversible capacity

Improving Cell-Level Safety

Li

Ni_xMn_yCo_z

Li

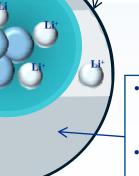
Ni_vMn_vCo_z

· Nano-particle circuit breaker, flame-retardant electrolytes, and cathode coatings to increase the thermal stability of the cell.

Goal: no fire or flame, even under abuse.

Providing Ultra High Specific Energy

- · Silicon-composite anodes to significantly improve capacity; elastomeric binders and nanostructures to achieve ~200 cycles
- Novel lavered oxide cathode with lithium-excess compositions ($Li[Li_xNi_vMn_zCo_{1-x-v-z}]O_2$) to improve capacity





Li-Ion Cell Development



NASA In-House Efforts

GRC

- Si-based Composite Anode Development
- Separator Assessments
- Cell Development
- Cell Integration
- Analytical and Thermal evaluations
- Modeling

IPL

- Layered Metal Oxide Cathode Development
- High Voltage, Flame Retardant Electrolyte Development

ISC

Safety Assessments

NASA Research Announcement Battery Cell Component Development Contracts

- · NEI Corp., "Mixed Metal Composite Oxides for High Energy Li-ion Batteries"
- University of Texas at Austin, "Development of High Capacity Layered Oxide Cathodes"
- · Physical Sciences, "Metal Phosphate Coating for Improved Cathode Material Safety"
- Yardney, "Flame-retardant, Electrochemically Stable Electrolyte for Lithium-ion Batteries"
- · Lockheed Martin Space Systems Company, "Advanced Nanostructured Silicon Composite Anode Program"
- · Georgia Tech Research Corp. & Clemson University, "Design of Resilient Silicon Anodes"
- · Giner, "Control of Internal and External Short Circuits in Lithium-Ion Batteries"

Component Scale-up and Cell Design and Development

Saft America

Leveraging

- NASA SBIR/STTRs
- NASA EPSCoR

- Interagency Advanced
 NASA Innovative **Power Group**
 - Partnership Program

NASA

Anodes

- Goal: 1000 mAh/g at C/10 (10 hour discharge rate) and 0°C
 - Over 3 times the capacity of SOA Li-ion anodes
 - Threshold value = 600 mAh/g at C/10 and 0°C

Technology Challenges	Current Approaches to Address
Minimize volume expansion during cycling	 Pursuing various approaches to optimize the anode structure to accommodate volume expansion of the silicon Nano-structured Si composite absorbs strain, resists active particle isolation on cycling Incorporation of elastic binders in Si –graphite and Si-C matrices Improvement of mechanical integrity by fabricating structure to allow for elastic deformation
Minimize irreversible capacity loss	 Protection of active sites with functional binder additives Pre-lithiation approaches are possible Nano-structured Si resists fracture and surface renewal
Achieve 250 cycles	 Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life

Composite Anodes for Ultra-High Energy Batteries



Objective:

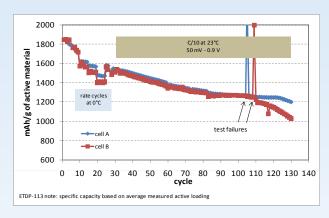
 Develop anode materials capable of delivering 1000 mAh/g at 0°C and C/10 (10 hour rate), and 200 cycles to 80% of their original capacity.

Accomplishments:

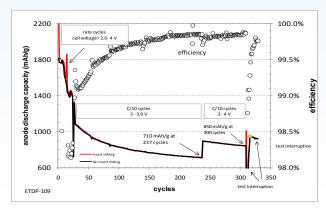
- Silicon anodes under development have demonstrated initial capacities of up to 1731 mAh/g.
- Novel silicon nanowire/carbon microfiber anode structure from Physical Sciences Incorporated produced over 1200 mAh/g for 110 cycles in room temperature testing at C/10 with good low temperature rate capability, achieving 83% of room temperature capacity at C/2 and 0 deg C.
- Full cell with Georgia Tech silicon anode and NCA cathode achieved satisfactory coulombic efficiency and maintained anode capacity above the threshold level of 600 mAh/g for over 200 cycles in an un-optimized cell.

Current Challenges:

- Specific capacity fade rates are still too high to meet the goal of 200 cycles at the cell level.
- Irreversible capacity is extremely high (>106% over 2 cycles in final contract deliverable)
- Limited capacity utilization after first cycle presents issue for positive electrode capacity matching
- Demonstrating performance at 0 deg C.



Cycle performance of PSI anode



Cycle performance of Georgia
Tech anode

Cathodes



· Goals:

- Specific capacity of 280 mAh/g at C/10 and 0°C to 3.0 V
- High voltage operation to 4.8 V
- Improved thermal stability over conventional Li-ion cathodes

Technology Challenges	Current Approaches to Address
High specific capacity at practical discharge rates	•Vary stoichiometry to determine optimum chemical formulation •Reduce particle size •Experiment with different synthesis methods to produce materials with physical properties such that their specific capacity is retained on production scale
Low volume per unit mass	 Vary cathode synthesis method to optimize properties that can: Improve energy density Improve ability to cast cathode powders Facilitate incorporation of oxide coatings, which have the potential to increase rate capability and reduce capacity fade to extend cycle life
Minimize 1st cycle irreversible capacity loss and irreversible oxygen loss	•Surface modification via coatings to improve cathode-electrolyte interfacial properties •Improves capacity retention •Reduces capacity fade

Cathodes



Objective:

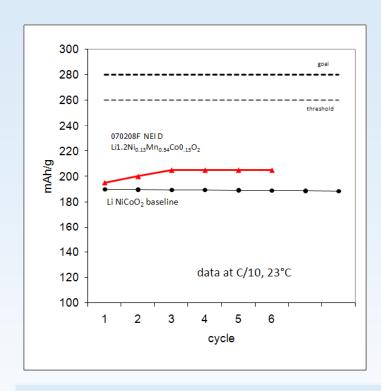
• Develop cathode materials with improved thermal stability and specific capacity (to 3.0V)>280 mAh/g at C/10 and 0°C.

Accomplishments:

- Synthesized high voltage materials with significant gains in specific capacity and rate capability
- •Tap density issues have been addressed increased to 1.6 2 g/cc but specific capacity to 3.0V degraded (from 252 mAh/g to ~210 mAh/g)
- Surface modified samples demonstrate higher capacity, lower irreversible capacity loss, and more cycle stability than unmodified cathode sample.

Current Challenges:

- Low temperature(0°C) capacity
- Address rate capability issues
- High first cycle irreversible capacity loss -~30% at RT
- Scale up and coating of large batches of materials needs to be demonstrated



Cathode Specific Capacity (mAh/g)- at C/10 Rate

Sample	23℃	0°C
UT Austin	231	208
NEI-D (UT Austin scaled up by NEI)	209	188

Electrolytes

 Goal: Develop flame-retardant and/or non-flammable electrolytes that are stable up to 5V

Technology Challenges	Current approaches to address
Electrolyte that is stable up to 5V	Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes
Non-flammable or flame retardant electrolyte	Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance
High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system)	Combine flame retardant additives with electrolyte formulations with high voltage stability. Operate systems to high voltages and investigate impacts on rate capability, specific energy, energy density and life.
Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and electrolyte-wetting.	Develop electrolytes that are not excessively viscous to ensure that the ionic conductivity is sufficiently high over the desired temperature range and the electrolyte-wetting is adequate.

Electrolyte



Objective:

• Develop flame retardant electrolytes for Liion cells that are stable up to 5.0 volts and maintain electrochemical performance.

Approach:

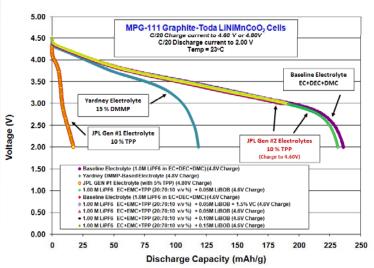
- Determine best formulation for lowflammability that is consistent with highvoltage mixed-metal-oxide cathodes, and with graphite and silicon composite anodes:
 - Vary concentration of triphenyl phosphate additives
 - Test both linear and cyclic fluorinated carbonates as non-flammable solvents.

Accomplishments:

- JPL Gen #1 Electrolyte has <50% heat release,
 <25% pressure rise, and >33% faster flame extinction compared to Saft electrolyte, but showed poor compatibility with NMC cathodes.
- JPL Gen #2 electrolytes (containing LiBOB) shows good performance with graphite/NMC electrodes, and has lower flammability because of increased TPP content (10%).

Description	Electrolyte	Percentage Flame Retardant Additive (%)	SET, S	Standard Deviation
Yardney/URI GEN # 2 Electrolyte	1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
JPL Electrolyte	1.0M LiPF6 in EC/EMC/TPP (2/6.5/1.5) + 2% VC	15% TPP	3.78	1.2
JPL Electrolyte	1.0M LiPF6 in EC/EMC/TPP (2/7/1) + 2% VC	10% TPP	9.57	0.9
JPL GEN #1 Electrolyte	1.0M LiPF6 in EC/EMC/TPP (2/7.5/0.5) + 2% VC	5% TPP	22.45	2.3
"Baseline" Electrolyte	1.0M LiPF6 in EC/EMC (3:7)	None	33.4	3.4
Yardney/URI GEN # 1 Electrolyte	1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

Developmental electrolytes exhibit lower Self-extinguishing time (SET) in flammability tests .



Electrochemical performance is maintained with JPL Gen #2 electrolyte

Separators



Goals:

- Identification of Li-ion cell separator materials that are compatible with the ETDP chemistry and provide an increased level of safety over SOA Li-ion cell separators
- Current efforts are focused on assessment of developmental (i.e., company IRAD materials) and commercial separator materials

Technology Challenges:

- Design optimization for high porosity and low ionic resistance to facilitate ionic conductivity while maintaining mechanical strength
- Must "shutdown" cell reactions below 130°C without shrinking or losing mechanical integrity

Significant results to date:

- Baseline separator identified (Tonen E20) and evaluated
 - · Physical, thermal, electrical and mechanical properties measured and documented
- Several promising commercial and IRAD materials identified and evaluated.
 - Physical Sciences, Inc.

Tonen polyethylene (PE)

· Exxon Mobil

Celgard polypropelene (PP)

Kynar PVDF resins

- Celgard PP/PE/PP trilayer
- Porous Power Technologies Symmetrix separators
 Saft America\

Safety



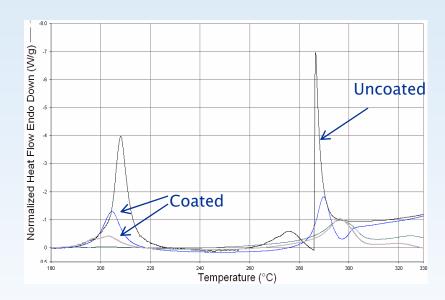
· Goal: Cells that are tolerant to electrical and thermal abuse

Technology challenges	Approaches to address
Safe electrodes	 Develop materials to improve tolerance to an electrical abuse condition Approach 1: Develop a high-voltage stable (phosphate) coating on cathode particles to increase the safe
	operating voltage of the cell and reduce the thermal dissipation by the use of a high-voltage stable coating material (cobalt phosphate).
	 Approach 2: Develop a composite thermal switch to shutdown cell reactions safely using coatings on the current collector substrates
Safe electrolyte	•Development of advanced high voltage, non- flammable/flame-retardant electrolytes (via electrolyte task)

Safety

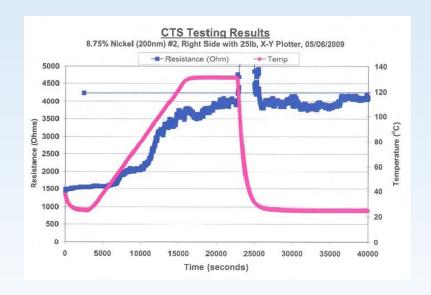


Physical Sciences - Coated Cathodes



- Successfully coated TODA 9100 NMC
- Demonstrated reduced isotherms with coated Toda 9100
- Coated materials have higher capacity, higher tap density, lower irreversible capacity, and better cycling stability

Giner - Composite Thermal Switch



- Unoptimized materials with composite coating on current collector exhibits switching behavior at >60 °C.
- Unable to demonstrate consistent, repeatable switching behavior to date

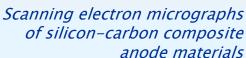
NASA

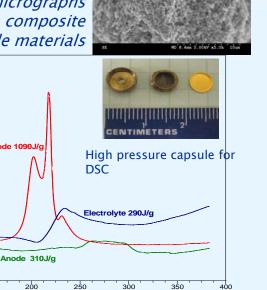
Analytical and Thermal Safety Evaluations

- Analytical studies to assess component structures, particle size and distribution, morphology, elemental composition, electrode purity, etc.
- Characterization of thermal behavior of cell components by Differential Scanning Calorimetry (DSC)
 - Separators
 - Electrolytes
 - Electrodes harvested from fully charged cells
- Characterization of thermal stability of cells and components by Accelerating Rate Calorimetry (ARC)



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DSC analysis on anode, cathode, and electrolyte

Accelerating Rate Calorimetry





Blast enclosure and control rack of the Thermal Hazards Technology ARC

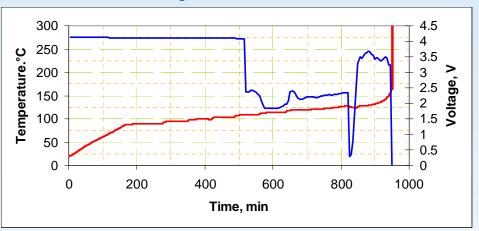


Positive terminal of new cell

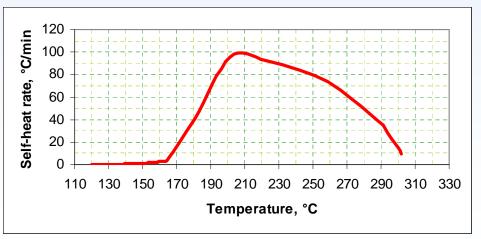


Positive terminal of vented cell

ARC data and voltage of Panasonic 18650 cell (100% SOC)



ARC/Self-heat data of Panasonic 18650 Li-ion cell (100% SC



The cell went into thermal runaway at 160°C with a maximum heating rate of 95.87°C/min. at 200°C

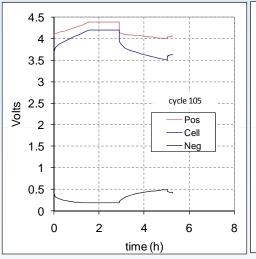
Cell Integration

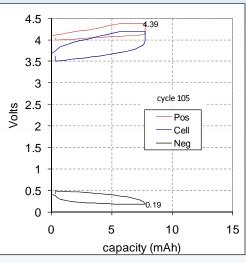


Objectives

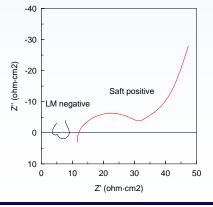
- Assess performance of integrated components
- Determine anode:cathode materials balance
- Predict full cell performance
- Determine formation procedures to maximize performance
- Determine optimum cycling parameters and cycling limitations
- Identify and understand performance and compatibility issues

Full cell testing with LM Si-based anode and Saft LiNiCoAl cathode





Increasing polarization at the cathode observed over 100 cycles

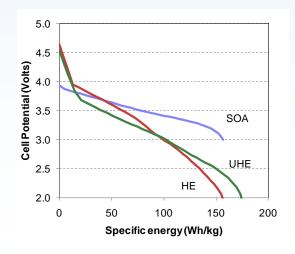


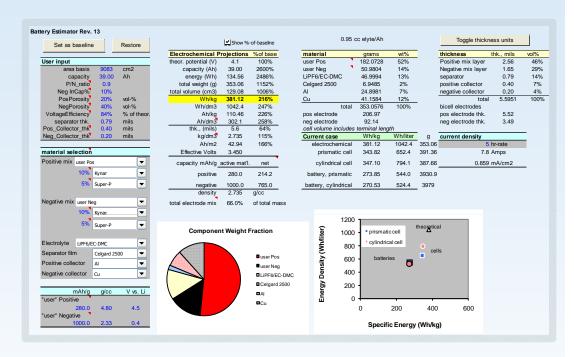
Electrochemical impedance after 100 cycles – Cathode impedance is greater than anode impedance, Si-based anode shows inductive loop

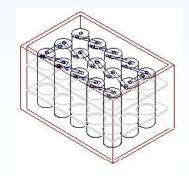
NASA

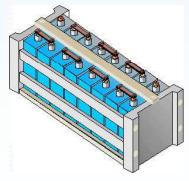
Cell/Battery Modeling

- Spreadsheet-based models project cell and battery level characteristics
- Tool for "what if?" analysis
- Rate performance can be estimated from laboratory data for electrodes under relevant conditions







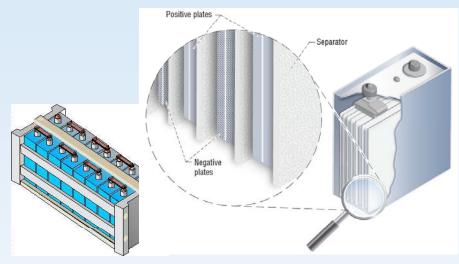


Cell Development Contract with Saft America



Contract Tasks:

- · Component screening and evaluation
 - Build and test electrodes and screening cells
 - Provide manufacturing perspective and feedback to component development efforts
- Scale-up promising NASA-developed components
- •Transition components from the lab to the manufacturing floor
- Optimize electrode parameters
- Build and test evaluation cells (10 Ah):
 - -Determine component interactions
 - -Determine cell-level performance
- Optional Tasks
 - Design flightweight cells (35 Ah)
 - Fabricate flightweight cells



Accomplishments:

- Evaluated and screened cathodes, anodes, electrolytes from component developers
- Guided cathode development efforts to produce materials with suitable tap density
- Provided guidance to align materials selections and processing parameters with manufacturing considerations
- Conducted studies to address materials balance in cells
- Established parameters for initial DD evaluation cells
- Fabricated and delivered DD and 34P cells with baseline chemistry



Cell Testing and Evaluation

- Evaluate cells produced under contract with Saft America
 - DD cells
 - 34P, prismatic, ~35Ah cells
- Survey commercial technology options for products that address NASA goals
 - Obtain and evaluate commercial products against NASA KPP's
- Assessments include:
 - Cell characterization at projected rates and temperatures
 - Life testing
 - Safety Testing
 - Overcharge tolerance
 - Overdischarge tolerance
 - Overtemperature tolerance
 - · Crush test







Battery Related Efforts

- Li-Air System Initiating effort that addresses the development of a primary battery system to meet high energy needs (>1850 Wh/kg)
 - SBIR supported efforts to begin soon
- Human Rating Process for Li-Ion Batteries for Launch Vehicle applications
- NASA Engineering and Safety Center Battery Technology Discipline Advancing Efforts
- International Space Station Low Earth Orbit Life Test



PEM Fuel Cell Development

Fuel Cells - Technical Objectives and Approach



Objectives:

Increase system lifetimes (10,000 hours) and reduce system mass, volume and parasitic power for primary and regenerative fuel cells, and Enable the use of regenerative fuel cells including the use of high pressure (>2000 psi) reactants to reduce tankage mass and volume.

Focus is exclusively on Hydrogen/Oxygen Proton Exchange Membrane fuel cells and regenerative fuel cell systems

Technical Approach is to develop:

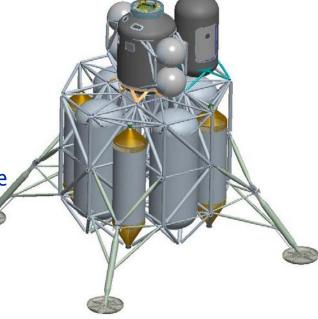
"Non-flow-through" proton exchange membrane stack and balance-of-plant technology;

Advanced membrane-electrode-assemblies for both fuel cells and electrolyzers.

Balanced high-pressure electrolyzers; and

Thermal and reactant management technologies for electrolyzer/fuel-cell integration into regenerative





Benefits of Non-Flow-Through Technology

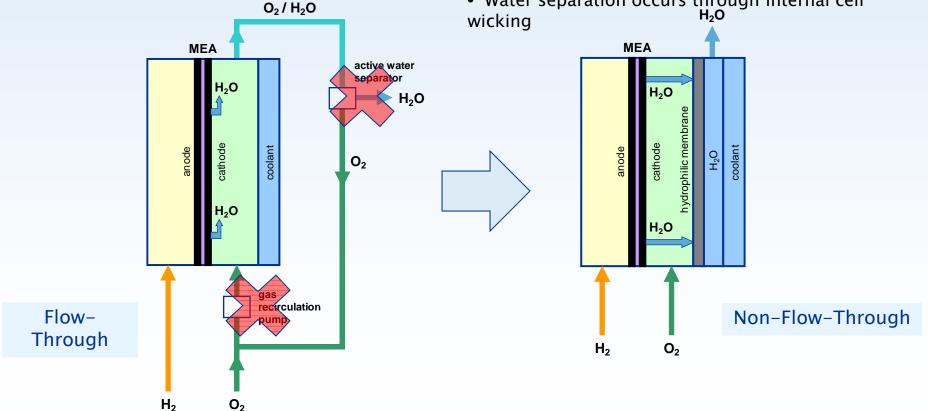
Technical approach: Develop "non-flow-through" proton exchange membrane fuel cell technology for a system improvement in weight, volume, reliability, and parasitic power over "flow-through" technology.

Flow-Through components eliminated in Non-Flow-Through system include:

- Pumps or injectors/ejectors for recirculation
- Motorized or passive external water separators

Non-Flow-Through PEMFC technology characterized by dead-ended reactants and internal product water removal

- Tank pressure drives reactant feed: no recirculation
- Water separation occurs through internal cell



Key Performance Parameters for Fuel Cell Technology Development

Customer Need	Performance Parameter	SOA	Current	Threshold	Goal**
		(alkaline)	Value*	Value**	(@ 3 kW)
			(NFT PEM)	(@ 3 kW)	
	System power density				
	Fuel Cell	49 W/kg	44 W/kg	88 W/kg	136 W/kg
Altair:	RFC (without tanks)	n/a	n/a	25 W/kg	36 W/kg
3 kW for 220 hours continuous, 5.5 kW peak.	Fuel Cell Stack power density	n/a	51 W/kg	107 W/kg	231 W/kg
	Fuel Cell Balance-of-plant mass	n/a	2 kg	21 kg	9 kg
Lunar Surface Systems:	MEA efficiency @ 200 mA/cm ²				
TBD kW for 15 days	For Fuel Cell	73%	72%	73%	75%
continuous operation	Individual cell voltage	0.90V	0.89V	0.90V	0.92V
Rover: TBD	For Electrolysis	n/a	83%	84%	85%
	Individual cell voltage	n/a	1.48	1.46	1.44
*Based on non-flow-through test hardware with 4-cells and heavy end plates, scaled to 3 kW	For RFC (Round Trip)	n/a	60%	62%	64%
	System efficiency @ 200 mA/cm ²				
**Threshold and Goal values based on full-scale (3 kW, 300 cm²) fuel cell and RFC technology.	Fuel Cell	71%	64%	71%	74%
	Parasitic penalty	2%	8%	2%	1%
Includes high pressure penalty on electrolysis efficiency 2000 psi	Regenerative Fuel Cell	n/a	n/a	43%	54%
	Parasitic penalty	n/a	n/a	10%	5%
	High Pressure penalty	n/a	n/a	20%	10%
Maintenance-free lifetime	Maintenance-free operating life				
Altair: 220 hours (primary)	Fuel Cell MEA	2500 hrs	13,500 hrs	5,000 hrs	10,000 hrs
Surface: 10,000 hours	Electrolysis MEA	n/a	n/a	5,000 hrs	10,000 hrs
(RFC)	Fuel Cell System (for Altair)	2500 hrs	n/a	220 hrs	220 hrs
	Regenerative Fuel Cell System	n/a	n/a	5,000 hrs	10,000 hrs

Technology Development for Fuel Cell and Regenerative Fuel Cell Systems



Pressure Accumulator

Pressure Transducers

Solenoid Valves



Balance-of-Plant: developing universal system to test cells from many vendors, and lightweight, low power system for demos.

Focus is reliable, 10,000 hours, operation

Pressure Regulator Pressure

Transducers

Fuel Cell Stacks from multiple vendors incorporate advanced water removal, thermal management, and manufacturing processes



Electrolysis development focuses on balanced, high pressure operation



NASA Test facilities (GRC, JSC, JPL) augment industrial capability



Pressure

Regulator

MEA development addresses system efficiency.

gov

Vendor Partners in Fuel Cell Development



Non-Flow-Through Fuel Cell Stacks

- Infinity baseline stack technology
- ElectroChem
- Proton
- Teledyne
- EIC, Giner membranes
- Lynntech catalysts

Electrolysis Stacks

- Hamilton Sundstrand (active liquid feed)
- Giner (active liquid feed, vapor feed)
- Infinity (vapor feed)
- · Sustainable Innovations (passive liquid feed)
- Electrochem (liquid feed)

Cross Cutting Stack Developments

Electrochem (coatings)

Passive Thermal Control

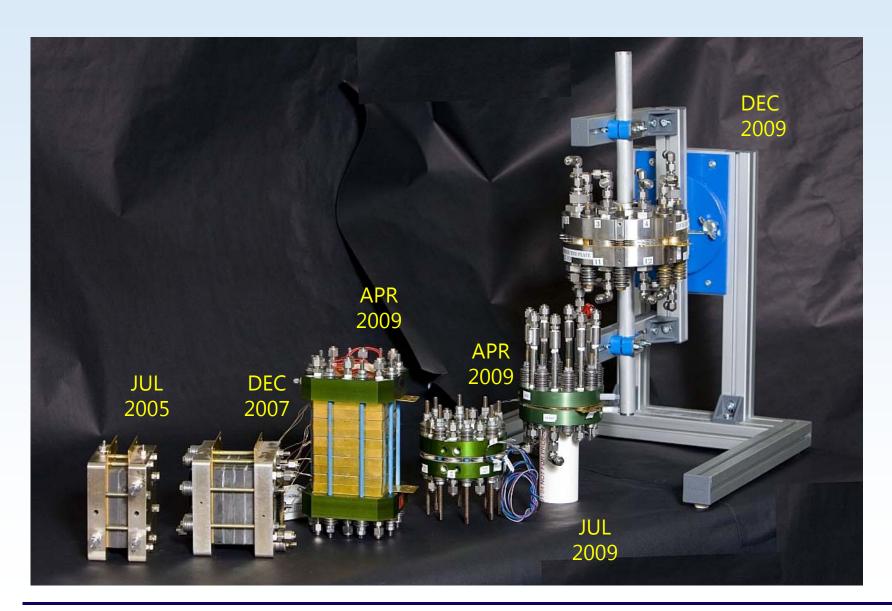
Thermacore (titanium flat-plate heat pipes)

Electrical Control

Ridgetop (integrated circuit development for extreme environments)



Infinity Non-Flow-Through Fuel Cell Stack Progression



Non-Flow-Through Fuel Cell Performance Demonstrated in Full Size (150cm2) Hardware

Key Accomplishments:

- 4-cell, 150 cm² non-flow-through fuel cell stack incorporating advanced manufacturing process demonstrated 100 hours of continuous testing
- Performance exceeded all prior small area (50 cm2) stacks.

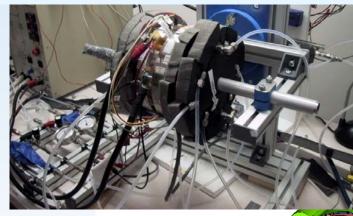
Significance:

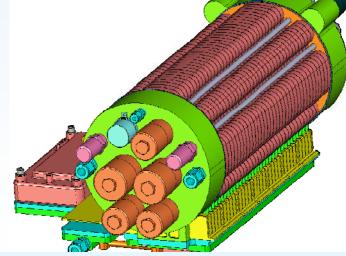
- Demonstrates the feasibility of non-flow-through fuel cell technology for Exploration missions
- Eliminates a substantial program risk associated with scale-up of non-flow through fuel cell technology from a laboratory size to the final flight hardware active area.
- Validates the decision to develop non-flow-through fuel cell technology over the previous flow-through technology.
- The 150 cm² cell size is optimum for full-size stacks anticipated for 120VDC Exploration missions

Future Work:

 Build ¼-scale breadboard, then 3-kW Engineering Model

Lab-scale non-flow-through fuel cell stack under test



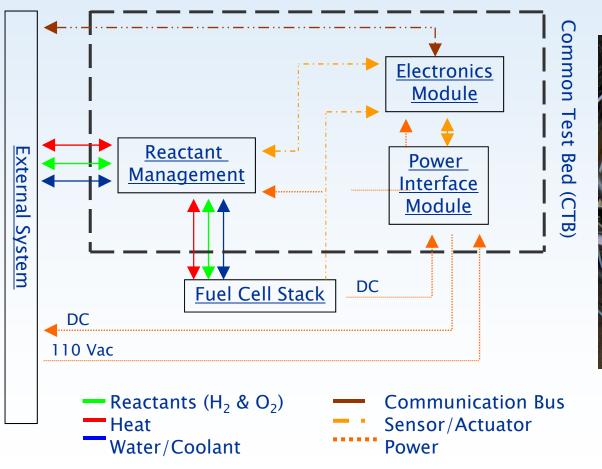


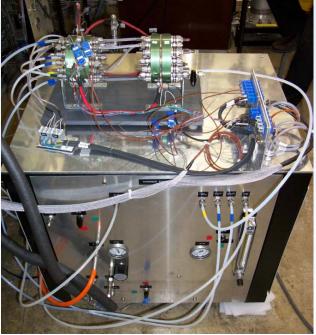
Schematic image of future 3kW non-flow-through fuel cell stack

Non-Flow-Through Fuel Cell Common Test Bed



- Configurable to test stacks provided by multiple vendors
- Capable of testing total output power of 1 kWe
- Capable of testing stacks up to 40 cells
- Capable of conducting un-attended life testing
- Developed and built using COTS hardware

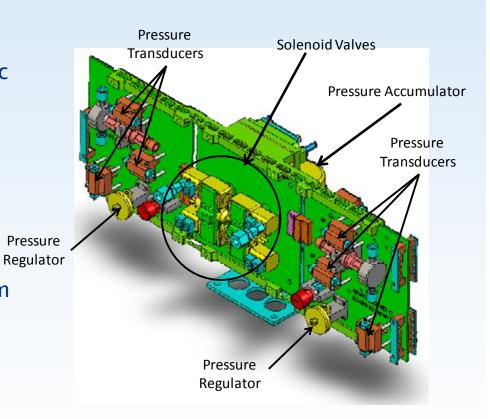




NASA

Integrated Balance-of-Plant Components for Fuel Cells

- Integrated balance-of-plant demonstrated in conjunction with the laboratory scale fuel cell stacks
- Balance-of-plant ran on a battery source consuming less than 10 watts of parasitic power to operate the fuel cell system
- Project that a full-scale (3-kW fuel cell system) balance-of-plant will operate on less than 50 watts of parasitic power
 - Significant reduction from flowthrough systems -
 - A 2-12 kW flow-thru fuel cell system tested at GRC required hundreds watts of parasitic power during operation
- That difference in parasitic power translates to significant reductions in reactant mass over the course of a mission



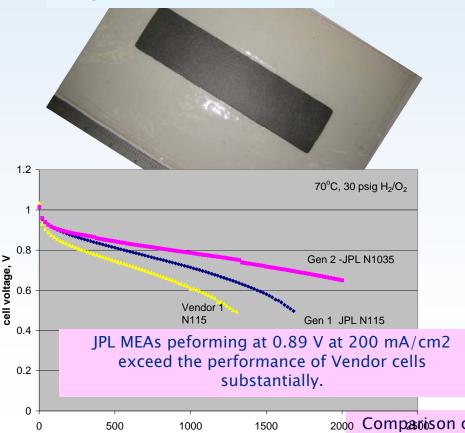
42 www.nasa.gov

Membrane Electrode Assembly Accomplishments: MEA performance exceeds minimum success criteria

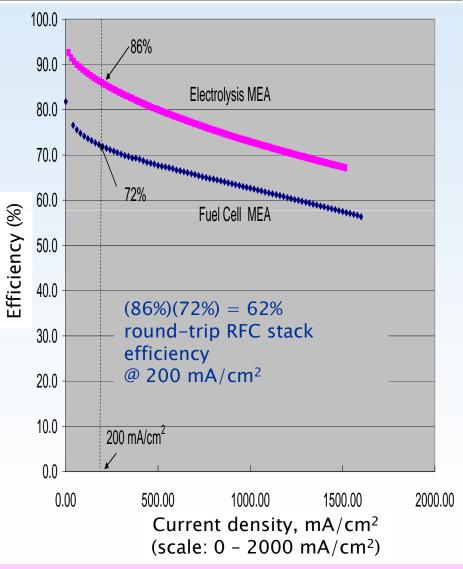


 NASA fuel cell and electrolysis MEA performance exceeds best performance of industry vendors

> JPL MEAs supplied to Teledyne, Infinity, and Proton Energy



current density, mA/cm2



Companison of JPL's best iridium-doped ruthenium with the latest vendor supplied MEA shows substantially better (30 mV) performance by the NASA material.

MEA and Electrolysis Technology

NASA

Objective:

Develop balanced high-pressure ($\geq 2,000$ psi) electrolysis technology for Exploration missions. Incorporate advanced membrane-electrode-assemblies (MEAs) with better electrical performance into high-pressure electrolyzers.

Accomplishment:

- JPL-developed MEA 86% efficient at 1.48V
- Hamilton Sundstrand modified existing International Space Station electrolyzer (liquid-feed) for high-pressure operation.
- Testing at JPL showed good voltage performance to 2000 psi H2 and 1000 psi O2 with Nafion MEA.

Significance:

- Advanced electrolysis MEAs will deliver more H2 and O2 gases with less electrical power input, reducing the required size of a solar array for a regenerative fuel cell system.
- Balanced high-pressure operation permits operation within an architecture having smaller tanks, reducing launch mass and volume requirements

Future Work:

• Vapor-feed and passive liquid-feed electrolyzers are being investigated to reduce the significant parasitic power draw of the pumps and water/gas separators required for liquid feed systems.

High-pressure electrolyzer in test stand



83 cm² MEA with platinumblack catalyst on hydrogen side and iridium oxide catalyst on oxygen side



Passive Cooling Plates Developed and Demonstrated

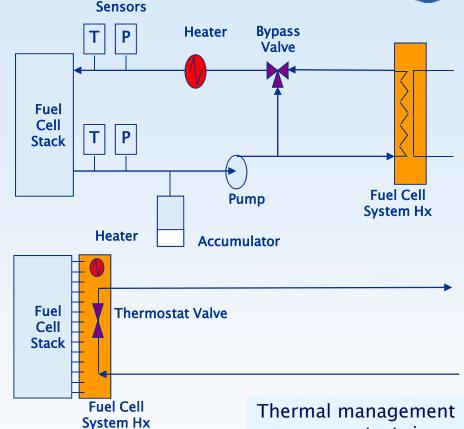
Passive cooling plates replace internal active pumped-liquid cooling loop resulting in reduced mass and volume, lower parasitic power, increased reliability, longer life

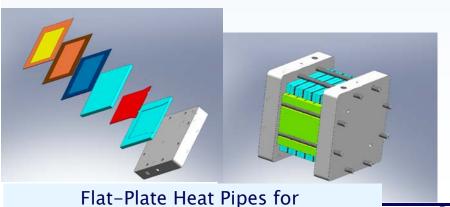
Pyrolytic graphite cooling plates have 4x the conductivity of copper

Flat-plate heat pipes have 30-40x the conductivity of copper

Conventional **Fuel Cell with Pumped Loop Thermal Management**

Fuel Cell with Passive Thermal Management





4-Cell TRL-4 Non-Flow-Through Stack

Temperature Distribution Across Pyrolytic Graphite Cooling Plates In 6-Cell Sub-kW Flow-Through Stack

vacuum test rig









"Passive BOP"



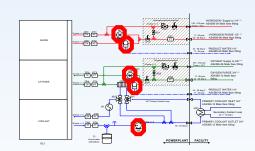
"Passive BOP" PEM



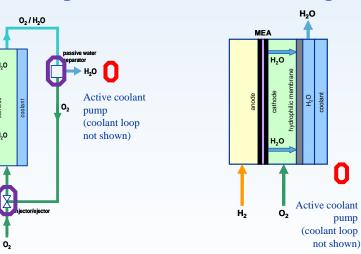
Flow-Through



Non-Flow-Through



Flow-Through



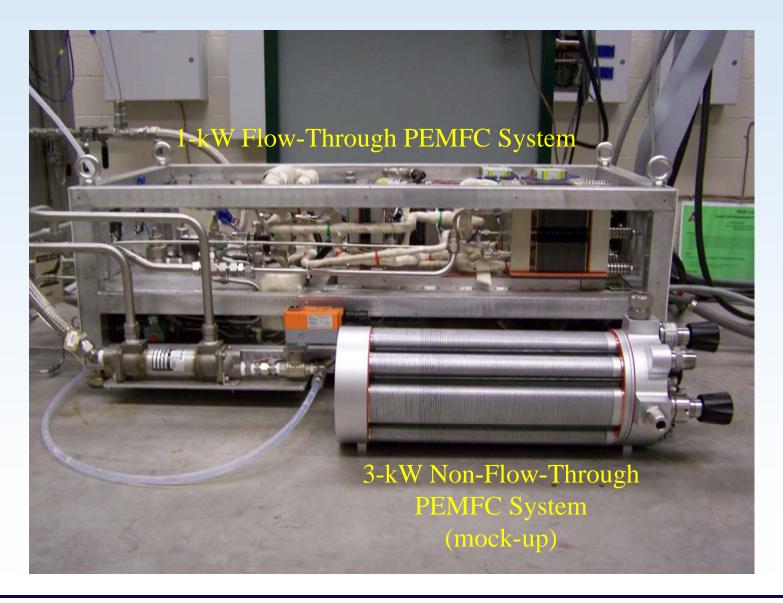
Active Mechanical Component (pump, active water separator)

Passive Mechanical Component (injector/ejector, passive water separator)

Fuel Cell Technology Progression to Simpler Balance-of-Plant

NAISA

PEMFC System Comparison



Fuel Cell Predicted Performance



- **Test data shows** that even with existing heavy endplates, power density of current hardware nearly matches that of SOA Shuttle alkaline flight hardware:
 - 59 kg non-flow-through stack (endplates 17 kg) + 10 kg BoP @ 3 kW = 44 W/kg
 - SOA Shuttle alkaline @ 6 kW = 49 W/kg
- Note: KPP threshold and goal power density values are based on 300 cm² hardware (for 30V systems), which is more mass efficient than smaller 150 cm² hardware (for 120 V systems). Our current expectations for 3kW performance are based on test results from 4-cell stacks, and assume a 4-screen design, 4 kg flightweight endplates, and a 10 kg BOP. The expected 3 kW performance ranges from:
 - 66 W/kg for the stack and **54 W/kg** for the system, assuming a 4-chamber cell (separate cavities for coolant and product water); to
 - 125 W/kg for the stack and **88 W/kg** for the system, assuming a 3-chamber cell (combined water/coolant cavity) and additional mass optimization.
- Next steps are to build successively taller stacks to move toward 1/4 scale breadboard (40 cells, 1 kW, 150 cm2) while retaining the excellent power density
- Voltage, lifetime, and some mass KPP's not specifically addressed in current fiscal year
 - Optimization for voltage not in current year scope, although some conductive coatings will be investigated
 - Lifetime testing not in current year scope
 - Mass optimization not in current year scope, although replacing metallic porous plate with Supor membrane for mass reduction will be investigated



Fuel Cell Related Efforts

- Unique SOFC design innovation for fuel cell and electrolysis systems is being pursued at GRC
 - Bi–Supported Cell Technology
 - Operate with High Specific Power 1kW/kg
- Hydrogen Infrastructure for Renewable Energy

Hydrogen Infrastructure for Renewable Energy



- •Renewable Hydrogen Today: Phase 1 of A Clean Energy Program for Economic Development
 - Deploy a hydrogen powered fuel cell RTA bus
 - Build a hydrogen refueling station at GLSC
 - Convert Lake Erie water into hydrogen using an electrolyzer powered by GLSC wind and solar

Technologies

- Proton-exchange-membrane (PEM) fuel cells
- High-pressure PEM electrolyzers
- Hydrogen refueling station system development
- System deployment

Outcomes

• Design study completed; awaiting additional funding for system development and deployment

Partners

• NASA GRC, GLSC, OAI, RTA, CSU, Sierra Lobo, Parker Hannifin, Hamilton Sundstrand, UTC; numerous other collaborators and funders



Artist's conception of an articulated hydrogen fuel cell bus in front of the Great Lakes Science Center, Cleveland, Ohio



RPC Electrochemistry Branch Facilities and Capabilities

Electrochemistry Branch - Batteries









Capabilities

- Fundamental electrochemical research – component development and characterization with state-ofthe-art analytical test capability
- Cell/Battery Design
- Cell/Battery Performance and Life Testing
- Cell/Battery Safety Testing
- Battery Performance Modeling
- Environmental Testing

Facilities:

- Development Laboratories SOA equipment for materials and component development, and analytical and electrochemical characterization
- •600 ft² Dry room with 1% relative humidity for handling moisture sensitive materials used in lithium based batteries
- •State-of-the-art battery cycling facilities with >100 independent test channels, 1-200 Ahr, 1-50 V
- •Environmental chambers to evaluate performance as a function of temperature (-75 °C to +200 °C)
- Accelerating Rate Calorimeter

NASA

Electrochemistry Branch Fuel Cells and Regenerative Fuel Cells

Capabilities

- Fundamental electrochemical research component development and characterization with state-of-the-art analytical test capability
- Design and development of fuel cell and regenerative fuel cell systems, including ancillary components and reactant storage systems
- · Fuel Cell System Modeling
- Fuel Cell System Performance and Life Testing and Evaluation







Fuel Cell Facilities

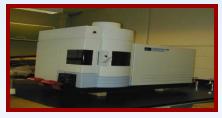
- •Fuel Cell Development Laboratories with SOA equipment for materials and component development, and analytical and electrochemical characterization capabilities
- •Fuel Cell Testing Laboratory 3 test cells for large-scale (up to 125kW) fuel cell and regenerative system evaluation and life testing, 2 independent control rooms
- Regenerative Fuel Cell Test Facility component and system design evaluation

Electrochemistry Branch Facilities









<u>Imaging and Material Analysis Laboratory -</u>

Surface and Thermal Analysis Capability

- Inductively Coupled Plasma Optical Emission Spectrometer
- Scanning Probe Microscope
- Scanning Electron Microscope Energy Dispersive Spectrometer
- Stereomicroscope
- BET Surface Area Analyzer

Thermal and Material Analysis Laboratory

Molecular analysis, particle size distribution, thermal property analysis

- Differential Scanning Calorimeter
- Fourier Transform IR Spectrometer
- Thermogravimetric Analyzer (TGA)
- Raman Spectrometer
- Particle Size Analyzer









Concluding Remarks

- ETDP/Energy Storage Project is a prime example of successful intercenter collaborations in the development of electrochemical systems
 - Relationships built and fostered working on joint projects provide sound basis for future work
- GRC capabilities and expertise compliment and reinforce capabilities at other NASA Centers
- Current project serves as model for teaming to advance energy storage technologies